Gas-Phase Heteroaromatic Substitution. 8.[1] Electrophilic Attack of Ethyl Cation on Pyrrole, *N*-Methylpyrrole, Furan, and Thiophene

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Abstract: Ethyl cation, obtained in the dilute gas state, together with CH_5^+, from the γ-radiolysis of methane, has been allowed to react with pyrrole, *N*-methylpyrrole, furan, and thiophene, in the pressure range 50–760 Torr and in the presence of variable concentrations of a gaseous base (NMe_3). The mechanism of the substitution and of the subsequent isomerization of the relevant ionic intermediates is discussed, and the intrinsic positional selectivity of the $C_2H_5^+$ ions is evaluated. Gas-phase $C_2H_5^+$ ion attack on pyrroles is characterized by a significant positional selectivity toward those substrate positions with the highest net negative charge (N:α:β = 13%:10%:77% for pyrrole; α:β = 19%:81% for *N*-methylpyrrole). Interaction of $C_2H_5^+$ with the furan center having the maximum value of the negative charge, i.e. the O atom, favors occurrence of α-substitution (α:β = 57%:43%). Thiophene displays no significant positional discrimination (α:β = 54%:46%). Gas-phase attack of $C_2H_5^+$ on simple five-membered heteroaromatics is mainly governed by electrostatic interactions established within the encounter pair. This characterizes gaseous $C_2H_5^+$ as a very "hard" electrophile, rather than a borderline acid, as expected on the grounds of the alkyl cation "hardness" scale. This deviation is explained in terms of the bridged geometry for $C_2H_5^+$ and its effect on the LUMO energy level of the ion.

In the preceding article of this issue,[1] it has been shown that the intrinsic orienting properties of simple five-membered heteroaromatics, such as pyrrole, may represent a suitable experimental probe for assaying the electronic features of gaseous charged electrophiles. While alkylating species such as t-$C_4H_9^+$, i-$C_3H_7^+$, and $CH_3FCH_3^+$ behave in the gas phase as typical "hard" electrophiles, attacking preferentially the ring positions of five-membered heteroarenes with the highest net negative charge (e.g. the β carbons of pyrrole), the CT_3^+ cation is found to act as a much "softer" Lewis acid, adding predominantly to the ring positions of the same substrates with the highest HOMO π-electron density (e.g., the α-carbons of pyrrole). Such peculiar behavior of methyl cation among alkylating reactants has been related to the energy level of the LUMO orbital of the electrophile, which increases in the reported "hardness" order $CH_3^+ < C_2H_5^+ < i\text{-}C_3H_7^+ < t\text{-}C_4H_9^+$.[2,3] While the significant energy gap between the LUMO of t-$C_4H_9^+$ (and i-$C_3H_7^+$) and the HOMO of five-membered heteroarenes leads to charge-controlled interactions in the relevant transition state, the use of a gaseous electrophile with a lower lying LUMO, such as CH_3^+, decreases the HOMO–LUMO energy gap to the point that the corresponding transition-state energy barrier is mostly determined by significant frontier-orbital mixing in the encounter pair.

Given the above "hardness" order for alkylating carbocations,[2,3] it is now desirable to ascertain whether this reactivity model applies as well to the ethyl cation, $C_2H_5^+$, which might be expected to behave toward simple five-membered heteroaromatics as a Lewis acid with a borderline character lying between that of the "soft" CH_3^+ and the "hard" i-$C_3H_7^+$ ion (eq 1).

(1)

Y = NH (1); NMe (2); O (3); S (4)

Experimental Section

Materials. Methane, oxygen, and trimethylamine were research grade gases from Matheson Co., with a minimum purity of 99.99 mol %. Pyrrole, *N*-methylpyrrole, furan, and thiophene were research grade chemicals from Fluka AG. These compounds were analyzed by gas chromatography (GLC) to check for the absence of alkylated impurities. 2-Ethylfuran and 2-ethylthiophene, required as GLC standards, were purchased from Aldrich Co. Isomeric ethylpyrroles, ethyl-*N*-methylpyrroles, 3-ethylfuran, and 3-ethylthiophene were prepared according to established procedures[4] and purified by preparative GLC. Their purity was checked by GLC analysis on a Perkin-Elmer 8320 gas chromatograph, equipped with a flame ionization detection (FID) unit, on the same columns employed for the analysis of the irradiation mixtures, and their identities were verified by conventional ^1H NMR spectroscopy.

Procedure. The general procedure used for the preparation of the gaseous mixtures and their irradiation have been described in detail elsewhere.[5] Typical experimental conditions were as follows: methane, 50–760 Torr; heteroaromatic substrate, 0.5–2.0 Torr; O_2, 4 Torr; NMe_3, 0–10 Torr. The radiation dose, as measured with a neopentane dosimeter,[6] was 3 × 10^4 Gy, delivered at the rate of 1 × 10^4 Gy h^{-1}, for all samples at 37.5 °C in a ^{60}Co γ-cell (Atomic Energy Canada Ltd.). Control experiments, carried out at a dose of 1 × 10^5 Gy, revealed no significant differences in the relative yields of products and their isomeric composition, at least within the range of doses covered.

Product Analysis. The analysis of the products was carried out by injecting measured portions of the irradiated reaction mixture into a Perkin-Elmer 8320 gas chromatograph, equipped with a FID unit. In order to avoid selective losses of the products by adsorption on the glass walls of the vessel, the analysis was repeated after washing the bulb walls with freshly purified ethyl acetate. Satisfactory agreement between the results from the gaseous mixtures and those from the ethyl acetate solutions was found in all runs. The irradiation products were identified by comparison of their retention volumes with those of authentic standards. Their yields were determined from the area of the corresponding elution peaks, with use of appropriate calibration curves for the detector response.

Computational Details. Standard quantum mechanical calculations, with the GAUSSIAN 80[7] set of programs, were performed in order to

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[1] Part 7: Angelini, G.; Sparapani, C.; Speranza, M., preceding paper in this issue.

[2] (a) Klopman, G. *Chemical Reactivity and Reaction Paths*; Klopman, G., Ed.; Wiley: New York, 1974. (b) Houk, K. N.; *Acc. Chem. Res.* **1975**, *8*, 361. (c) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976. (d) Ho, T. L. *Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic Press: New York, 1977.

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[6] (a) Lias, S. G.; Ausloos, P. *J. Chem. Phys.* **1965**, *45*, 2748. (b) Collin, G. J. *Can. J. Chem.* **1976**, *54*, 3050.

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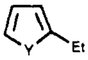
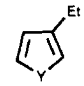
Table I. Product Yields from the Gas-Phase Attack of $C_2H_5^+$ Ions on Simple Heteroarenes

system composition[a] (Torr)			relative yields of products[b] (%)			
substrate	CH_4	NMe_3				total absolute yield[c] (%)
1 (0.61)	50	–	22	69	9	84
1 (0.55)	150	–	24	68	8	61
1 (1.03)	300	–	25	66	9	43
1 (1.58)	500	–	26	67	7	33
1 (1.42)	760	–	23	72	5	27
1 (1.30)	760	2	11	76	13	7
1 (1.57)	760	5	10	77	13	3
1 (1.81)	760	10	10	77	13	1
2 (0.51)	50	–	30	70	–	28
2 (0.67)	150	–	28	72	–	19
2 (0.71)	300	–	28	72	–	13
2 (0.68)	500	–	29	71	–	11
2 (1.03)	760	–	29	71	–	9
2 (1.00)	760	2	20	80	–	3
2 (1.57)	760	5	18	82	–	2
2 (1.39)	760	10	19	81	–	1
3 (0.81)	50	–	61	39	–	24
3 (0.67)	150	–	60	40	–	21
3 (0.60)	300	–	58	42	–	14
3 (0.98)	500	–	61	39	–	11
3 (0.85)	760	–	66	34	–	12
3 (1.03)	760	2	66	34	–	8
3 (0.87)	760	5	64	36	–	4
3 (2.01)	760	10	57	43	–	3
4 (0.58)	50	–	54	46	–	76
4 (0.76)	150	–	53	47	–	56
4 (1.48)	300	–	54	46	–	50
4 (1.56)	500	–	53	47	–	44
4 (0.98)	760	–	54	46	–	62
4 (1.23)	760	2	54	46	–	20
4 (1.67)	760	5	54	46	–	15
4 (1.51)	760	10	54	46	–	11

[a] O_2, 4 Torr; radiation dose, 3×10^4 Gy (dose rate, 1×10^4 Gy h^{-1}). [b] Ratio of the yield of each individual product to the combined yield of all products identified. Each value is the average of several determinations, with an uncertainty level of ca. 5%. [c] Absolute yields estimated by using the $G_{(C_2H_2^+)}$ value available from the literature (ref 11) (see text).

evaluate the 6-31G*[8] SCF eigenvalues of the LUMO orbitals for CH_3^+, $C_2H_5^+$, i-$C_3H_7^+$, and t-$C_4H_9^+$ carbocations. Optimized geometries, at the 6-31G* level of calculation, were taken from literature data.[9,10] C_{2v} symmetry was assumed for i-$C_3H_7^+$ and C_{3h} for t-$C_4H_9^+$. The LUMO energies have been evaluated as follows: CH_3^+ (ground −7.6 eV, vib excited −8.6 eV), $C_2H_5^+$, classical (open) form (−6.2 eV) $C_2H_5^+$ nonclassical (bridged) form (−3.8 eV), i-$C_3H_7^+$ (−5.1 eV), t-$C_4H_9^+$ (−4.6 eV).

Results

Gas-phase attack of ethyl cation, generated by γ-radiolysis of methane in the presence of a thermal radical scavenger (O_2, 4 Torr) on the selected heteroaromatic substrates **1**–**4** yields the corresponding ethylated derivatives, namely *N*-, α-, and β-ethylpyrrole (**5**, **6**, and **7**, respectively) from **1**, α- and β-ethyl-*N*-methylpyrrole (**8** and **9**, respectively) from **2**, α- and β-ethylfuran (**10** and **11**, respectively) from **3**, and α- and β-ethylthiophene (**12** and **13**, respectively) from **4**.

The relevant absolute yields and isomeric distributions of products are reported in Table I. The total absolute yields of the irradiation products are given as the percent ratio of their $G_{(M)}$ values, i.e., the number of molecules of product M formed per 100 eV of energy absorbed by the gaseous mixture, to the $G_{(C_2H_5^+)} = 0.9$ available from the literature.[11] The results of these calculations, while largely approximate,[12] represent nevertheless an estimate of the relative efficiency order of the reaction channel leading to the ethylation products. The ionic character of this substitution process is ensured by the presence of an effective thermal radical scavenger (O_2), contained in the gas at concentrations even higher than those of **1**–**4**, and confirmed by the dramatic decrease of the overall product yields caused by the addition to the gaseous mixture of 1.3 mol % of NMe_3, an efficient Brønsted acid interceptor.

Inspection of Table I reveals that β-ethylation of pyrroles **1** and **2** predominates under all conditions. The relative distribution of the ethylated derivatives, while rather insensitive to the total pressure of the system, appears to depend on the presence and the concentration of the added NMe_3 base. Addition of NMe_3 at atmospheric pressure leads to an increase of the relative yields of the β-substituted derivatives of **1** and **2**, which level off to 77% (**7** from **1**) and 81% (**9** from **2**) at the highest NMe_3 partial pressure (10 Torr). In the case of **1**, the increase of **7** in the presence of NMe_3 is paralleled by an increase of the N-ethylated product **5** and a decrease of the α-substituted derivative **6**, which level off to 13% and 10%, respectively. Gas-phase $C_2H_5^+$ ion attack on furan **3** and thiophene **4** leads to the preferred formation of the corresponding α-substituted products (**10** from **3**, and **12** from **4**), under all conditions. In the absence of NMe_3, the relative distribution of **10** from **3** increases from ca. 60 to 66% as the total pressure of the system increases from 50 to 760 Torr. At atmospheric pressure, it decreases again by addition of NMe_3 to

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(7) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Khan, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

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(9) Whiteside, R. A.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 1980.

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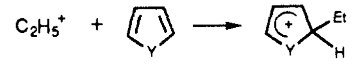
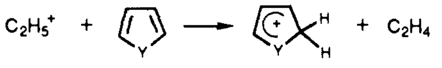
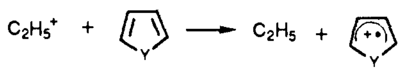
(11) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341.

(12) There are considerable uncertainties as to the radiation dose actually absorbed by the gas and to the pressure dependence of the known $G_{(C_2H_5^+)}$ values (ref 11). In addition, there are several reaction channels available to $C_2H_5^+$ ions following their attack on **1**–**4** that represent only one of the nucleophiles present in the irradiated systems.

Table II. Energetics of Several Relevant Reactions of $C_2H_5^+$ Ions with Heteroaromatic Compounds[a]

process	$\Delta H°$ (kcal mol^{-1}); Y = NH (**1**)	NMe (**2**)	O (**3**)	S (**4**)
2  **14**	−71	−78	−57	−57
3  **15**	−45	−52	−29	−33
4  **16**	−4	−11	+12	+11

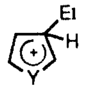
[a] The formation enthalpies of the ions and the neutrals, used for these calculations have been taken from ref 4 and from (i) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. (ii) Eland, J. H. D.; *Int. J. Mass Spectrom. Ion Phys.* **1969**, *2*, 471. An estimate of the $\Delta H_f°$ values of **14** can be arrived at by assuming that the proton affinities of the ipso position of ethylated heteroaromatics is equal to that of the corresponding unsubstituted substrates, taken from ref 4. Other conceivable reaction channels are thermochemically forbidden for all selected substrates.

level off to 57% at 10 Torr of the added base. In the case of thiophene **4**, the relative distribution of isomeric ethylated products (54% (**12**), 46% (**13**)) is largely independent of the pressure of the mixture and the NMe_3 concentration.

Discussion

Nature of the Ionic Reagent. The electrophile used in the present study is the gaseous $C_2H_5^+$ ion obtained together with the CH_5^+ from the γ-radiolysis of CH_4.[13] Use of a large excess (over ca. 100:1) of CH_4 over the heteroaromatic substrate ensures thermalization of the ionic species formed from the radiolysis by multiple unreactive collisions with the CH_4 precursor before attacking an heteroarene molecule. Thermal $C_2H_5^+$ ion ($\Delta H_f°$ = 215.6 kcal mol^{-1})[14] may act both as a Lewis and as a Brønsted acid by exothermically alkylating and protonating the selected substrates (Table II) whereas the accompanying CH_5^+ ion ($\Delta H_f°$ = 216.0 kcal mol^{-1})[14] reacts exclusively as proton donor. While the exothermic process 2 of Table II is recognized as the main source of the ethylated products of Table I, occurrence of the accompanying pathways 3 and, in part, 4 leading to products undistinguishable from the starting substrates may account for the limited absolute yields of the recovered derivatives (Table I).

The Alkylation Process. The results of the radiolytic experiments are consistent with the ethylation pattern 2 of Table II, involving the primary attack of a thermal ethyl cation on the heteroaromatic compound. The resulting ionic intermediate **14**, excited by the exothermicity of its formation process, undergoes collisional deactivation with the bath CH_4 molecules prior to neutralization by proton transfer to a gaseous base, such as NMe_3 or the substrate itself. In competition with collisional quenching, the excited heteroarenium ions **14** may undergo several secondary processes, including isomerization to a more stable structure or fragmentation with loss of ethylene. The latter process may represent an additional route to the protonated heteroaromatic **15**, which can be formed by direct proton transfer from $C_2H_5^+$ to the substrate as well (eq 3 of Table II). Its extent as well as that of the inter- and intramolecular isomerization of the ethylated intermediates **14** are expected to be minimized in the systems with the highest total pressure and NMe_3 concentration, where efficient collisional quenching and rapid neutralization of the primary ethylation adducts take place. In this view, the isomeric composition of the ethylation products recovered from the systems at 760 Torr and in the presence of 10 Torr of NMe_3 closely reflects the relative distribution of the primary O-ethylated intermediates from attack of $C_2H_5^+$ on the ring positions of the selected substrates. It follows that, in the kinetically controlled step of the ethylation process, the β-alkylated derivatives **17** of pyrroles **1** (Y = NH, 77%) and **2** (Y = NMe, 81%) and the α-alkylated ones **18** of furan **3** (Y = O, 57%) and thiophene **4** (Y = S, 54%) are preferentially formed. In the absence of the base NMe_3, a fraction of the primary N-ethylated intermediates from **1** is able to isomerize to the corresponding structure **18** (Y = NH), as demonstrated by the distinct decrease of the relative yield of *N*-ethylpyrrole **5** and the parallel increase of that of the α-substituted isomer **6**. Under the same conditions structure **18** from **1** (Y = NH) and **2** (Y = NMe) does not appear to rearrange further to its β-substituted isomeric form **17** (Y = NH, NMe). Instead, a 10% decrease of the relative yields of the β-ethylated products **7** from **1** and **9** from **2** is observed in the absence of NMe_3, which is attributable to a unimolecular fragmentation of **17** (Y = NH, NMe) under long-lived ion conditions, as previously suggested in related studies.[15]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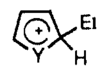
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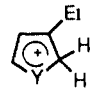
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A reaction pattern similar to that of pyrroles **1** and **2** is valid for the attack of $C_2H_5^+$ ions on furan **3** and thiophene **4**. Here the initial population of the C-alkylated intermediates **17** and **18** (Y = O, S) emerges directly from the isomeric distribution of their neutral derivatives (43% of **11** and 57% of **10** from **3**, 46% of **13** and 54% **12** from **4**) as measured under kinetically controlled conditions (atmospheric pressure in the presence of 10 Torr of NMe_3). The initial population of the heteroatom-ethylated intermediates, which may conceivably accompany formation of their C-alkylated isomers **17** and **18** (Y = O, S), cannot be directly determined, since they are expected to lose the ethyl moiety by interaction with a suitable acceptor (NMe_3). A rough estimate of the relative abundance of the heteroatom-alkylated intermediates can be inferred by a comparative analysis of the isomeric distribution of the ethylation products in Table I, measured at 760 Torr as a function of the NMe_3 concentration. By analogy with the results of previous related studies,[15] it is expected that as the lifetime of the heteroatom–ethylated intermediates from **3** (Y = O) and **4** (Y = S) is increased by lowering the NMe_3 concentration; there is a greater probability of isomerization to the more stable structure **18** (Y = O, S), as in the case of pyrrole **1**. The increase of the relative yield of **10** from **3** (from 57 to 66%) as the NMe_3 partial pressure decreases from 10 Torr to zero can be accounted for by intramolecular isomerization of the O-ethylated intermediate from **3** to the corresponding α-substituted

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(13) (a) Ausloos, P.; Lias, S. G. *Ion–Molecule Reactions*; Franklin, J. L., Ed.; Plenum: New York, 1972. (b) Ausloos, P.; Lias, S. G.; Scala, A. A. *Adv. Chem. Ser.* **1966**, *58*, 264. (c) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1964**, *40*, 1854.

(14) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(15) Laguzzi, G.; Speranza, M. *J. Chem. Soc., Perkin Trans. 2* **1987**, 857.

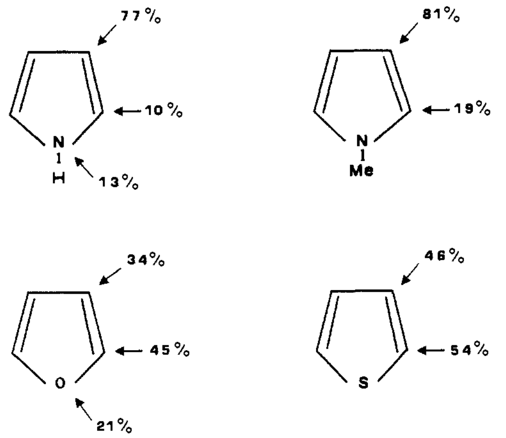

Figure 1. Positional selectivity of gaseous $C_2H_5^+$ ion toward simple heteroaromatic compounds.

form **18** (Y = O). In the absence of NMe_3, a decrease of the total pressure of the system with **3** leads to a reverse trend, with the relative yield of the β-substituted derivative **11** increasing at the expense of its α-isomer **10**. Such behavior may be explained, in agreement with previous conclusions concerning related investigation,[15] by a slower further isomerization of intermediate **18** (Y = O) to structure **17** (Y = O), prior to collapsing to the more stable form **19** (Y = O). With the reasonable assumption that at 760 Torr and in the presence of NMe_3, this latter **18** → **17** → **19** (Y = O) isomerization sequence is minimized, the increase of the **10**/**11** yield ratio from **3** would reflect the contribution by the rapid $O \rightarrow C_\alpha$ ethyl group transfer within the O-ethylated intermediates to the population of the heteroarenium ion isomer **18** (Y = O). On this basis, we can roughly estimate the relative extent of direct $C_2H_5^+$ ion attack on the oxygen of furan **3**, as approximately equal to 21%. The corresponding attack of $C_2H_5^+$ ions to the sulfur atom of thiophene **4** is comparatively ineffective, in view of the relative constancy of the isomeric distribution of its ethylated derivatives **12** and **13** under all experimental conditions. Accordingly, we can evaluate the intrinsic positional selectivity of the $C_2H_5^+$ ion toward furan **3** and thiophene **4**. The relevant figures, together with those of pyrroles **1** and **2**, are shown in Figure 1.

Positional Selectivity. The intrinsic site selectivity of gas-phase $C_2H_5^+$ cation towards the selected heteroaromatics **1**–**4** corresponds to the expected behavior of a typical "hard" electrophile. The site selectivity measured for $C_2H_5^+$, expressed by the β/α substitution ratio for pyrroles, exceeds that of other "hard" alkylating species by a factor of ca. 2.3.[15,16] The "hard" electrophile $C_2H_5^+$ is electrostatically directed toward the negative center of furan (**3**), i.e., the oxygen atom, yielding a "chelate" adduct, favoring subsequent attack at the adjacent α-center by proximity effect.[17] In the case of thiophene **4**, wherein any electrostatic interaction between the heteroatom and the electrophile is much less significant, the resulting positional selectivity is essentially determined by the negative charge density of the ring positions of the substrate, i.e., $\alpha > \beta > S$.[17]

If the intrinsic orienting properties of pyrroles **1** and **2** can be used to rank order gaseous ionic electrophiles in terms of their "hardness", the results of the present study place the "hardness" of gaseous $C_2H_5^+$ ions even higher than that of $CH_3FCH_3^+$, t-$C_4H_9^+$, and i-$C_3H_7^+$. An explanation for such a peculiar "hard" character of $C_2H_5^+$ can be found in the energy level of its LUMO orbital and its dependence upon the geometry of the ion. The $C_2H_5^+$ ion may exist as a classical (open) or a nonclassical (bridged) structure, whose relative stability has been the subject of considerable attention. There is now substantial theoretical evidence, based upon ab initio calculations,[18] that the preferred structure of the ethyl cation is bridged rather than open. While the open form of $C_2H_5^+$ has a low-lying LUMO orbital whose calculated energy (−6.2 eV) fits into those of the alkyl cation series, the bridged structure has a much higher LUMO orbital (−3.8 eV at the SCF 6-31G* level of calculation).

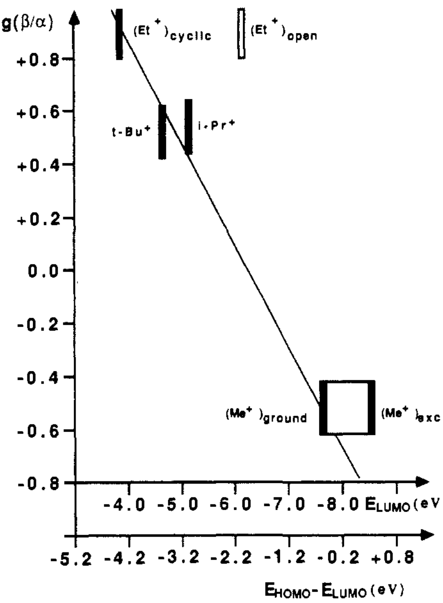

Figure 2. Plot of site selectivity of alkyl cations toward pyrrole **1**, expressed as the log [**7**]/[**6**] (log (β/α)), as a function of SCF 6-31G* calculated LUMO eigenvalues of the alkylating electrophile.

If the "hardness" of a cation can be related to the energy of its LUMO[2,3] a direct correlation should exist between the β/α ratio measured in the alkylation of **1** and the calculated LUMO energy of the electrophile. A linear correlation between log (β/α) and the calculated LUMO eigenvalues was found for CH_3^+, $C_2H_5^+$, i-$C_3H_7^+$, t-$C_4H_9^+$ only when the nonclassical form of the ethyl cation is considered (Figure 2). If the classical form of this ion is included in this plot, a large deviation from the linearity is observed. On these grounds and in agreement with previously reported indirect evidence,[19] it is concluded that gaseous ethyl cation exists as a stable nonclassical bridged structure, which places it at the top of the alkyl cations "hardness" scale, at variance with the normally reported t-$C_4H_9^+ > i$-$C_3H_7^+ > C_2H_5^+ > CH_3^+$ "hardness" order.[2,3]

Conclusions

The present study supports to the view that the gas-phase attack of $C_2H_5^+$ ions on simple five-membered heteroaromatics is essentially regulated by the electrostatic interactions established within the encounter pair. Such a conclusion is inferred from the kinetic predominance of the $C_2H_5^+$ ion attack on those pyrroles **1** and **2** position(s) with the highest net negative charge, i.e., the β-carbons and the heteroatom. The experimental site selectivity measured in this study allows one to draw a "hardness" order for simple alkyl cations, in which $C_2H_5^+$ is placed above the very "hard" electrophiles, t-$C_4H_9^+$ and i-$C_3H_7^+$, rather than in a borderline position between the "hard" i-$C_3H_7^+$ and the "soft" CH_3^+ ions. This deviation is explained in terms of the high LUMO of $C_2H_5^+$ with respect to those of the other alkylating species, due to the bridged structure of $C_2H_5^+$. In using absolute "hardness" as a tool for predicting the reactivity of organic cations,[3,20] it is

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important to consider other features besides an empirical "hardness" scale based purely upon thermochemical methods,[8] where the order necessarily refers to alkyl cations with the same geometry of the alkyl moiety in their neutral precursors. A more general warning against thermochemical approaches to "hardness" scales for charged electrophiles stems from the observation that the chemical "hardness" concept is often used to weigh electron mixing in the transition state for Lewis acid–base reactions and its effect on the relevant energy level. Thus, one should not be surprised if the alkyl cation "hardness" scale derived from the present gas-phase kinetic investigation does not match the one empirically inferred from thermochemical considerations.

Registry No. 1, 109-97-7; **2**, 96-54-8; **3**, 110-00-9; **4**, 110-02-1; $C_2H_5^+$, 14936-94-8; CH_3^+, 14531-53-4; NMe_3, 75-50-3; *i*-$C_3H_7^+$, 19252-53-0; *t*-$C_4H_9^+$, 14804-25-2; 2-ethylpyrrole, 1551-06-0; 3-ethylpyrrole, 1551-16-2; *N*-ethylpyrrole, 617-92-5; 2-ethyl-*N*-methylpyrrole, 24037-61-4; 3-ethyl-*N*-methylpyrrole, 53871-25-3; 2-ethylfuran, 3208-16-0; 3-ethylfuran, 67363-95-5; 2-ethylthiophene, 872-55-9; 3-ethylthiophene, 1795-01-3.

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Radical Ions in Photochemistry.[1] Carbon–Carbon Bond Cleavage of Radical Cations in Solution: Theory and Application

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Abstract: The cleavage of radical cations of two series of alkanes, 1,1,2-triaryl- and 1,1,2,2-tetraarylalkanes, generated by photoinduced single electron transfer in acetonitrile–methanol, occurs with formation of radical and carbocation fragments. The radical cations of some unsymmetrically substituted alkanes cleave to give all four of the possible products, two hydrocarbons emanating from the radicals and two methyl ethers from the carbocations, in proportion to the oxidation potentials of the two possible radical fragments. There is an excellent linear correlation between the logarithm of the observed ratio of products and that calculated from the reported electrochemically determined oxidation potentials ($r = 0.998$, 5 points). The proportionality constant (1.27) for this relationship is close to unity which indicates that the product ratio is determined by the relative rates of cleavage in the two possible modes or by equilibration of the radicals and carbocations before separation of the geminate radical carbocation pair and not by equilibration upon reencounter of freely solvated radical and carbocation fragments. The effect of temperature on the relative oxidation potentials of the radicals studied is small and can be neglected when radicals of the same order (i.e., both secondary or both tertiary) and of similar size are compared. The ratio of products obtained upon cleavage of the radical cation at 25 °C can be used to determined standard oxidation potentials of radicals. The oxidation potential of the diphenylmethyl radical (0.350 V vs SCE) has been accepted as the primary standard and the (4-methylphenyl)phenylmethyl (0.265 V) and bis(4-methylphenyl)methyl (0.188 V) radicals are established as secondary standards against which the oxidation potentials of other radicals can be measured. Oxidation potentials of several 4-substituted cumyl radicals have been determined by this photochemical method. There is a good ($r = 0.987$, 5 points) linear correlation between the measured oxidation potentials and the σ^+ substituent constants. The reaction constant is appropriately negative and large ($\rho = -6$).

Several years ago we reported that irradiation of an acetonitrile–methanol (3:1) solution of methyl 2,2-diphenylethyl ether (**1**) and 1,4-dicyanobenzene (**2**) led to the formation of diphenylmethane (**3**) and the dimethyl acetal of formaldehyde (**4**) in high yield (reaction 1 in Scheme I).[2] Key steps in the proposed mechanism (Scheme II) involve formation of the radical cation of the ether by single electron transfer to the singlet excited state of **2**, followed by carbon–carbon bond cleavage of the resulting radical cation. No methyl diphenylmethyl ether (**5**) was detected. Apparently cleavage of the radical cation of **1** occurs with the exclusive formation of the diphenylmethyl radical and the α-oxycarbocation. The explanation offered for this regioselectivity was that cleavage occurred to give the carbocation of that radical fragment which had the lower oxidation potential. At the time the oxidation potential of the α-oxymethyl radical was not known. The value subsequently reported is compatible with this explanation. The oxidation potential of the diphenylmethyl radical (0.35 V vs SCE, all of the electrochemical potentials mentioned in this paper are relative to the saturated calomel electrode) is 0.6 V higher than that of the α-oxymethyl radical.[3]

There have been several recent reports which deal with this type of reaction, and the salient features of the originally proposed mechanism remain intact.[4,5] There are however several important points that require further clarification, and this paper deals primarily with two of them. (1) The reaction is *not* general—on what basis can reactivity be predicted? (2) Only two products are obtained upon cleavage of some radical cations, while all four

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